Co-Optimization of
Fuels & Engines

Multi-Mode: Fuel Kinetics

Chiara Saggese, Scott W. Wagnon, Goutham Kukkadapu, William J. Pitz (PI) (LLNL)

June 3, 2020

Project # ft075

2020 DOE Vehicle Technologies Office

Annual Merit Review

better fuels | better vehicles | sooner

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

LLNL-PRES-809198

Overview

Timeline

Project start date: 10/1/2015

Project end date: 9/30/2021*

Percent complete: 58%*

Barriers

Lack of fundamental knowledge about the fuel kinetics impact on multi-mode, mixing controlled compression ignition, and advanced compression ignition engine performance:

- Dilute Gasoline Combustion
- Low-Temperature Combustion
- Clean Diesel Combustion

Budget

Task	FY19	FY20
F.2.2.2 LLNL Pitz	$800K	$805K
F.2.2.6 LLNL Pitz		$150K
F.2.2.7a LLNL Pitz		$90K
F.2.2.6a LLNL Pitz		$60K

Partners

One industry awardee

External advisory board

Nine national labs

20+ universities

80+ stakeholder organizations

120+ researchers

*Start and end dates refer to the two three-year life cycles for DOE lab-call projects. Progress reflects the current three-year cycle.

Relevance: Barriers

"… robust lean-burn and EGR-diluted combustion technology and controls, especially relevant to the growing trend of boosting and down-sizing engines."

"… understanding of the impact of likely future fuels on low temperature combustion (LTC)…"

"Soot formation and oxidation processes … are not well enough understood to develop robust soot models for computational fluid dynamics (CFD)."

Barriers from the Advanced Combustion and Emission Control Roadmap, March 2018

Relevance: Objectives

Overall Co-Optimization of Fuels and Engines objective:

Deliver foundational science to develop fuel and engine technologies that will work in tandem to achieve efficiency, environmental, and economic goals

Task objectives

LLNL Kinetic mechanism development

Develop kinetic models for Co-Optima fuel blends that can be used to accurately predict combustion behavior at different engine operating modes including the effects of dilution, equivalence ratio, EGR, pressure, and temperature

Kinetic models to predict PAH and Soot

Develop PAH/soot models that predict the formation and oxidation of PAH/soot occurring in in Multimode, MCCI and ACI engine modes

Kinetic modeling of NOx promotion of autoignition

Develop kinetic models that accurately predict the promotion effect of NO to ensure accurate simulation of autoignition occurring in Multimode, Advanced Compression Ignition (MD/HD) and MCCI engine combustion.

Identify chemistry controlling synergistic blending

Identify chemistry that controls synergetic blending (e.g. hyperboosting) and the fuel structures (functional groups) that provide these benefits.

EGR: Exhaust Gas Recirculation. MCCI: Mixing Controlled Compression Ignition. MD: Medium Duty. HD: Heavy-Duty.

Milestones

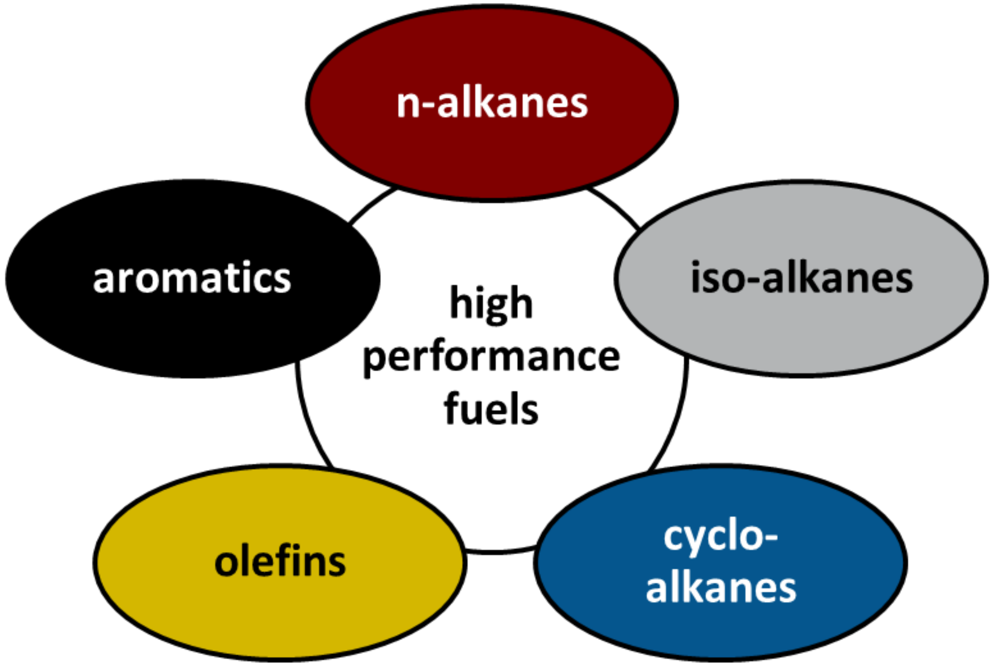
Month, Year	Description of Milestone or Go/No-Go Decision	Status
December, 2019	F.2.2.6: Validated NOx kinetic model that predicts iso-octane promotion by NO	Completed
March, 2020	F.2.2.2a: Develop/improve kinetic models for 2-3 blendstocks for multimode and ACI. Updated Co-Optima + HPFs base fuel model	Completed
March, 2020	F.2.2.6: Provide Co-Optima gasoline surrogate mechanism + HPFs with updated NOx submodel to AED & TK teams for evaluation	Completed
~~March, 2020~~ September, 2020	F.2.2.6a: Send identified molecular structures (functional groups) for phi sensitivity to HPF team	Delayed, on target
June, 2020	F.2.2.7a: Validated PAH/soot kinetic model that predicts soot measurements in laboratory flame burners	On target
September, 2020	F.2.2.2b: Develop/improve kinetic models for 2-4 blendstocks for multimode and ACI	On target

Blendstocks: Single component or multicomponent mixtures used to blend into a base fuel to achieve desired fuel properties. NOx: Nitric oxides. ACI: Advanced Compression Ignition. HPF: High-Performance Fuel. AED: Advanced Engine Development. TK: Toolkit Team. PAH: Polycyclic Aromatic Hydrocarbon.

Approach

F.2.2.2 – LLNL Kinetic mechanism development

> Develop chemical kinetic mechanisms for high performance fuels (HPFs) and their blends with base fuels (BOBs[1]). Validate kinetic mechanism over a range of temperature, pressure, equivalence ratio, EGR, and dilution relevant to engine combustion.



[1]BOB: Blendstock for oxygenate blending

Approach

F.2.2.7a – Kinetic models to predict PAH and Soot

> Improve and develop PAH kinetic model for HPF blendstocks and Co-Optima base fuels. Validate soot model by comparison to soot measurements in a shock tube by University of Central Florida (UCF).

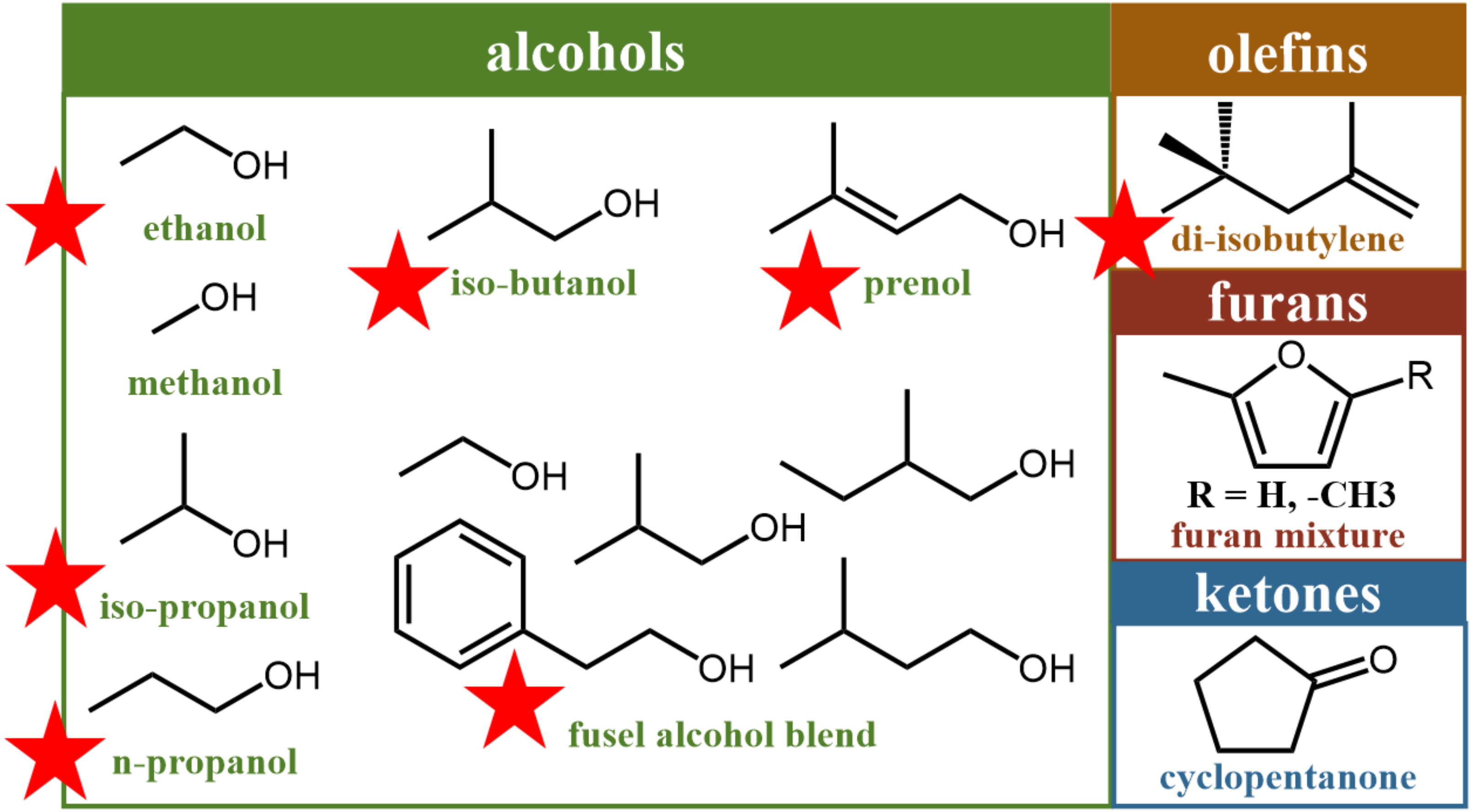
F.2.2.6 – Kinetic modeling of NOx promotion of autoignition

> Develop, improve and validate the chemical kinetic mechanism for NOx chemistry used for Co-Optima HPFs and BOBs over a range of NO concentration and temperature at engine-relevant pressures and equivalence ratios.

F.2.2.6a – Identify chemistry controlling synergistic blending and fuel structures that provide these benefits

> Use reaction path analysis, sensitivity analysis, and expert chemical kinetic knowledge to identify controlling chemistry for ACI fuel properties. Identify the fuel molecular structures (functional groups) that manifest this controlling chemistry.

Technical Accomplishments and Progress: Developed and improved kinetic models for blendstocks with highest merit function score



New or improved models for blendstocks on the list of the 21 most promising candidates for multimode[1]

Since the last DOE Annual Merit Review

7 new or improved kinetic models

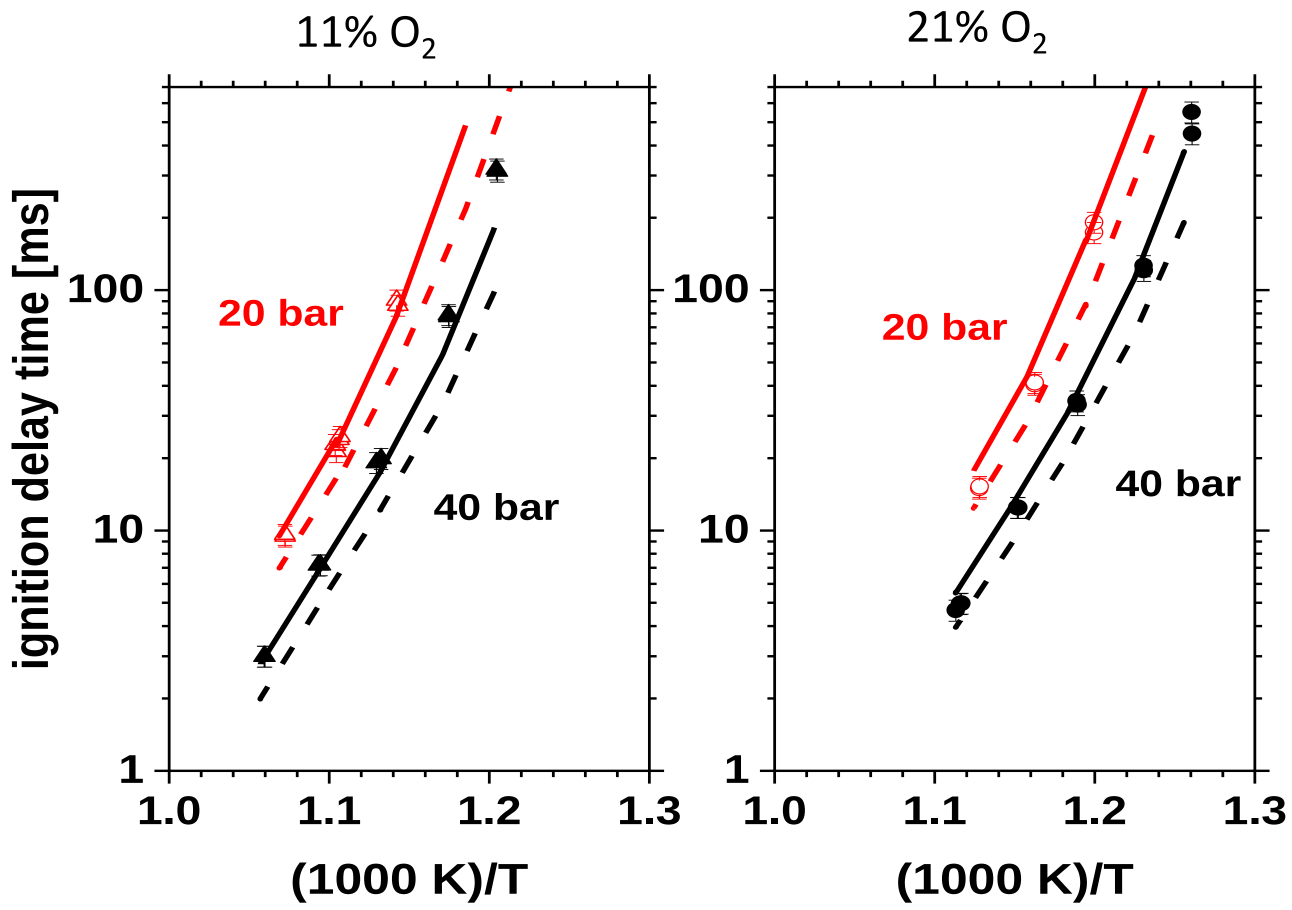
[1]NREL FY20 Q2 dashboard milestone

Technical Accomplishments and Progress: Improved kinetic model for ethanol

F.2.2.2 – LLNL kinetic model development

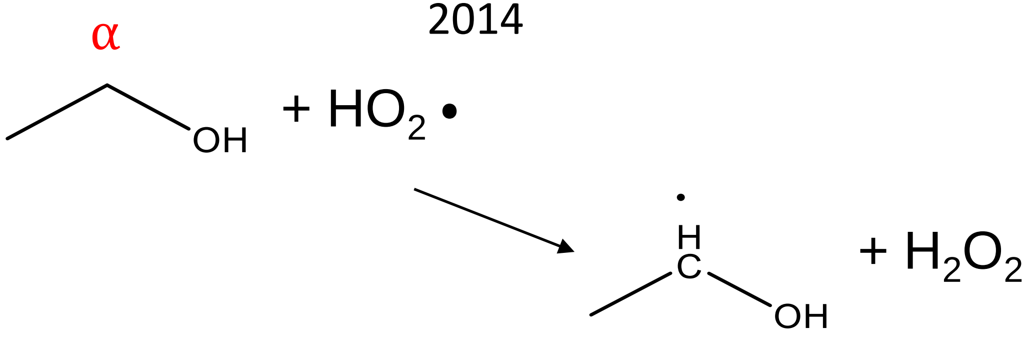
Ethanol with 11 and 21 % $O_2/N_2/Ar$, φ=1

- - Original model
— New model



Symbols: Rapid compression machine (RCM) experiments from ANL

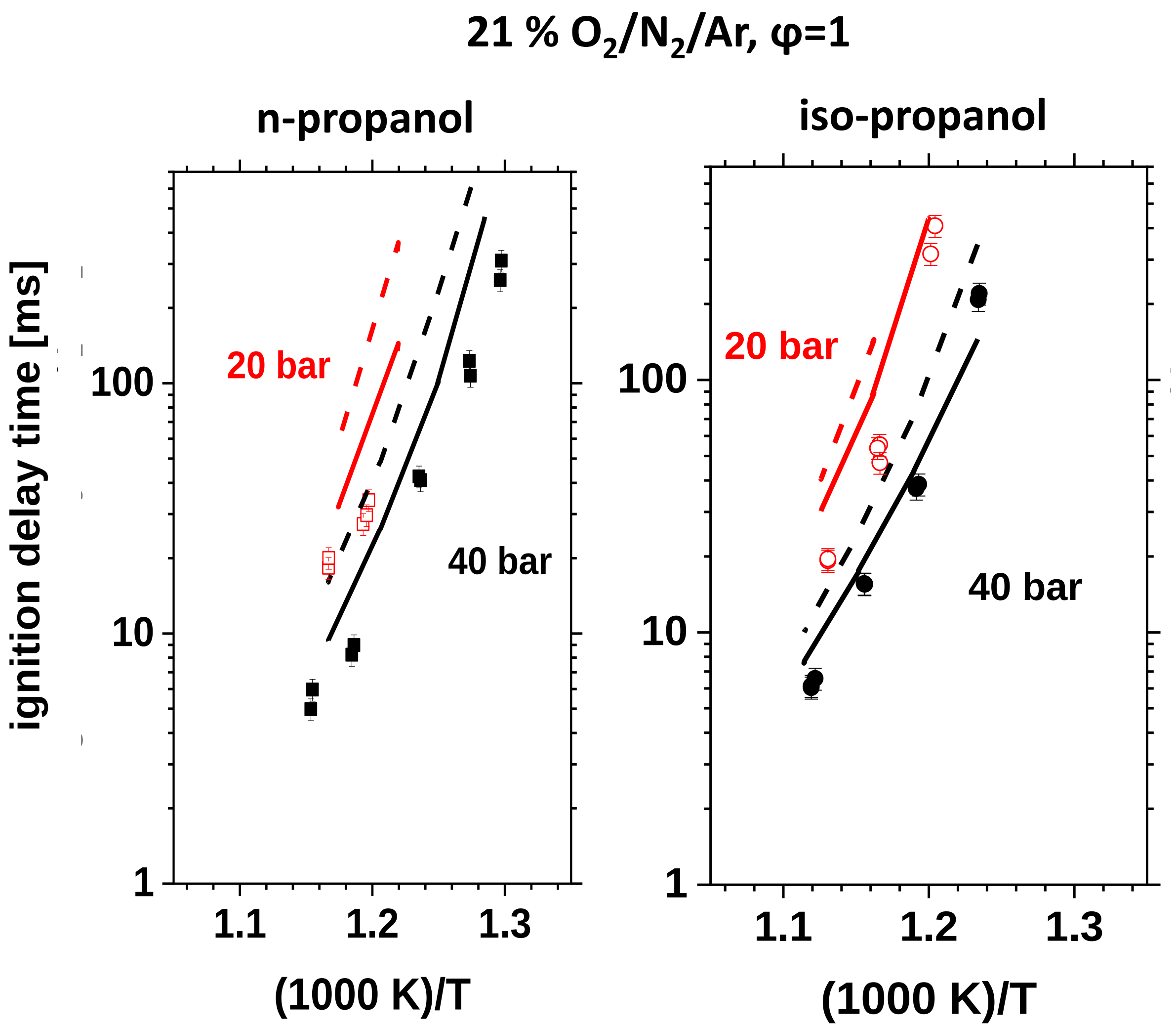
Sensitivity analysis showed that improvement likely due to using H-abstraction by HO_2• on α-site of ethanol from Mittal et al., Combust. Flame, 2014



Cheng, Goldsborough, et al., accepted for presentation 38th International Combust. Symp.

Technical Accomplishments and Progress: Improved kinetic model for propanols

F.2.2.2 – LLNL kinetic model development



- - Original model

— New model

<u>Symbols</u>: RCM experiments from ANL

<u>Lines</u>: Original and updated Co-Optima kinetic model

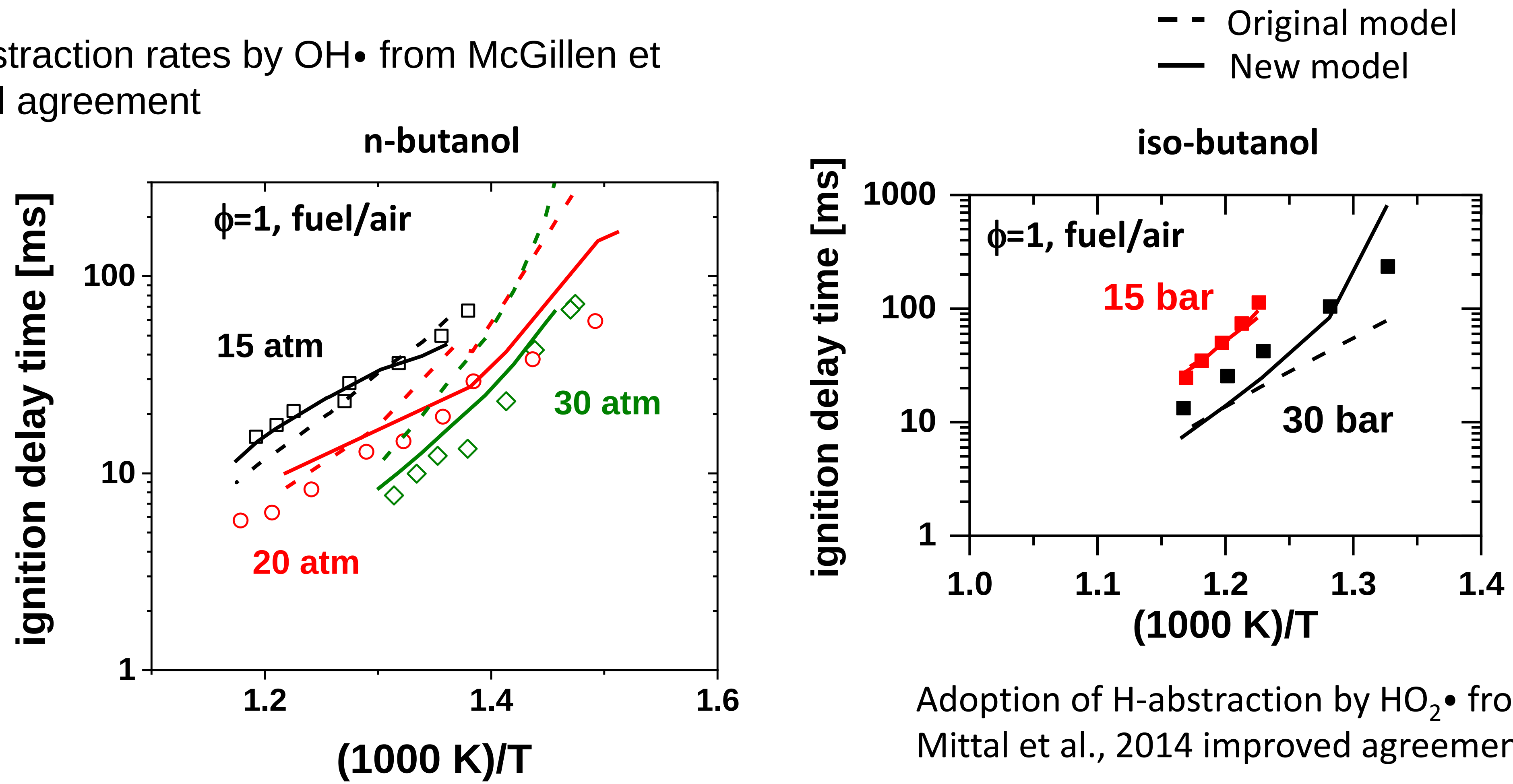
Adoption of H-abstraction rates by OH• from McGillen et al. 2013 and H-abstraction by HO_2• from Mittal et al., 2014 helped to improve agreement

S. Cheng, Goldsborough et al., accepted for presentation 38th International Combust. Symp.

Technical Accomplishments and Progress: Improved kinetic model for propanols

F.2.2.2 – LLNL kinetic model development

Adoption of H-abstraction rates by OH• from McGillen et al. 2013 improved agreement



Adoption of H-abstraction by HO_2• from Mittal et al., 2014 improved agreement

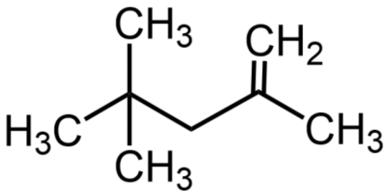
Symbols: RCM experiments from Weber et al. (2013) and Agbro et al. (2017)

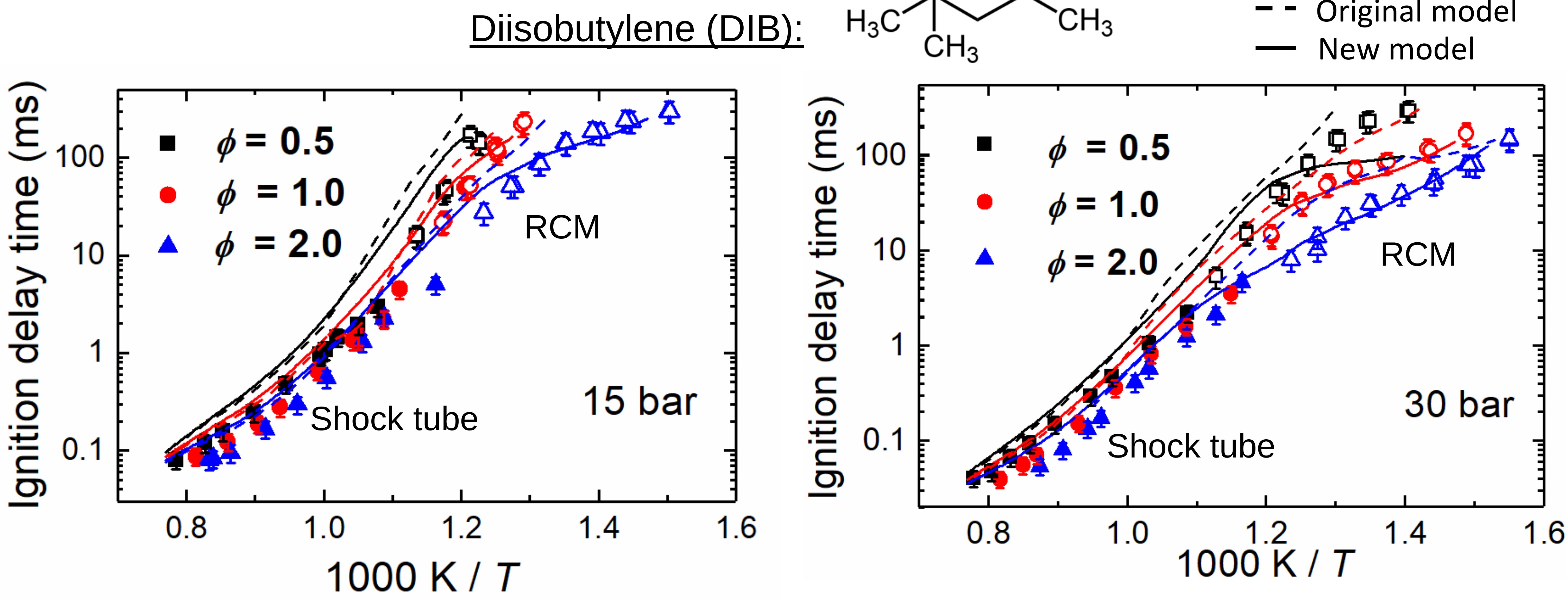
C. Saggese et al., accepted for presentation 38th International Combust. Symp.

Improved DIB model using RCM ignition data, JSR data, and flame speed data

F.2.2.2 – LLNL kinetic model development

Diisobutylene (DIB):





Symbols: New shock tube and RCM experiments from NUIG

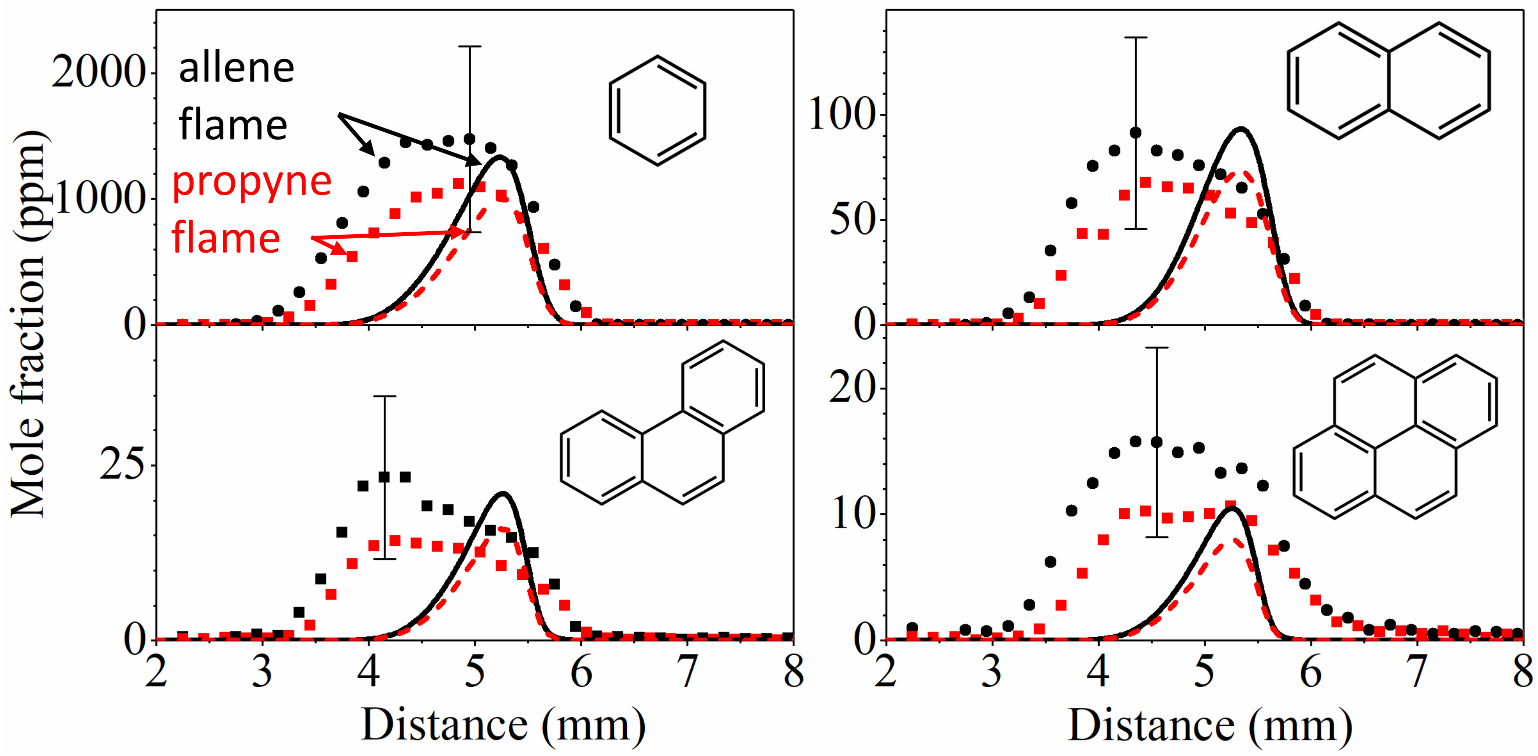
Lines: LLNL kinetic model

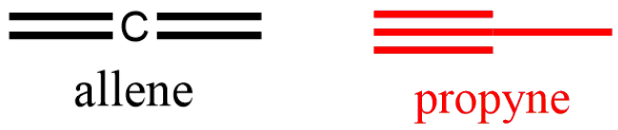
Collaborations with NREL, National University of Ireland - Galway (NUIG), University of Lille, & UCF to collect flow reactor, shock tube, rapid compression machine, and flame speed data

Technical Accomplishments and Progress: Improved PAH/Soot model

F.2.2.7a – Kinetic models to predict PAH and Soot

Simulated and measured aromatics and PAHs in allene (black) and propyne (red) counterflow flames:





Performance of mechanism benefited from recent understanding in PAH growth from:

- Phenyl radical + propargyl radical (Morozov & Mebel, PCCP, 2020)
- Phenyl radical+ allene/propyne (Mebel et al., Faraday. Discuss, 2016)

Symbols: SNL experiments

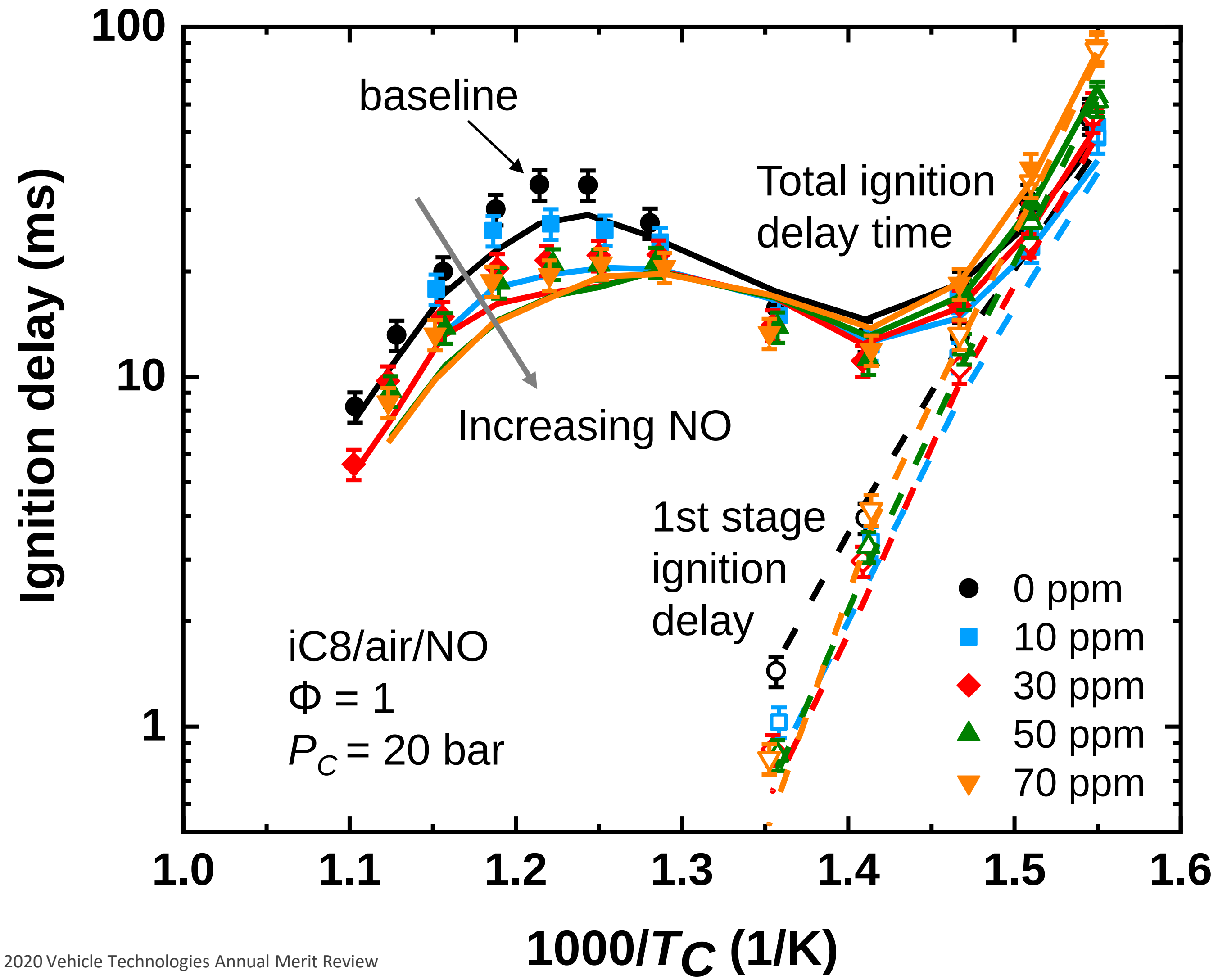
Lines: LLNL kinetic model

Experiments: Sandia counterflow, non-premixed flame burner, P= 0.92 atm

Kukkadapu, et al., accepted for presentation at the 38th Int. Combust. Symposium, (2020)

Technical Accomplishments and Progress: Improved/validated kinetics for NO promotion

F.2.2.6 – Kinetic modeling of NOx promotion of autoignition



Symbols: RCM data from UCONN
Lines: LLNL kinetic model

Added the most up-to-date NOx model, which is Glarborg et al. (PECS 2018)

Also reaction classes like RH+NO2, RO2+NO and R+NO2 where R is a fuel radical

Subcontract with University of Connecticut:

UCONN UNIVERSITY OF CONNECTICUT

R. Fang et al., Spring Technical Meeting of the Eastern States Section of the Combustion Institute, March, 2020

Responses to Previous Year Reviewers' Comments

Most reviewer comments were positive:

"The reviewer indicated that chemical kinetics underpin combustion, auto-ignition, and pollutant formation. Therefore, understanding reaction kinetics and having a robust means of describing and predicting them is fundamentally important to developing advanced fuels and advanced engines. The relevance of this activity is very high, and it is an essential, enabling component of the overall Co-Optima research effort."

More critical comments:

Reviewer comment: "The reviewer would like to have seen MD and HD issues listed in a more prominent position on the list of future research. "

Response: Advanced Compression Ignition (MD/HD) is included in future work for FY21.

Reviewer comment: "The reviewer said that there were good collaborations within the Co-Optima team, but the reviewer would like to have seen more collaborations outside of this space."

Response: We have many collaborations with universities outside of the Co-Optima team.

Collaboration and Coordination with Other Institutions

Collaboration with seven national laboratories ANL, LLNL, NREL, ORNL, PNNL, SNL

Goldsborough; Som; Lapointe; McNenly; Pitz; Whitesides; Fioroni; McCormick; Splitter; Szybist; Bays; Dec; George; Hansen; Mueller; Pickett; Sjoberg; Skeen

Four Co-Optima university partners

Massachusetts Institute of Technology > Model development; theoretical calculations

Pennsylvania State University > Yield sooting index (YSI) predictions using kinetic models

University of Central Florida > Experiments for kinetic model validations

Yale University > YSI measurements

One subcontract by LLNL

University of Connecticut (by LLNL) > Experiments for kinetic model validations

Universities outside of Co-Optima

King Abdullah University of Science and Technology > Experiments; calculations

National University of Ireland – Galway > Experiments; modeling; calculations

Politecnico di Milano > Modeling

University of Lille > RCM experiments; calculations

University of Michigan > Experiments

Lund University > flame speed measurements

Industry

Advanced Engine Working Group

Coordinating Research Council

General Motors

Coordination

Monthly team and stakeholder meetings

Quarterly leadership planning meetings

Annual all-hands meeting

Remaining Challenges and Barriers

Validating chemical kinetic models over wider pressure ranges, equivalence ratios, EGR dilution levels, and blends

Experimental measurements of EGR mixtures, including NOx

Studies that expand our knowledge of particulate matter precursor formation and ability to predict soot formation and oxidation

Modeling and measurements of research grade fuels for multi-mode (SI/ACI), mixing controlled compression ignition, and medium- and heavy-duty advanced compression ignition engine operation

Proposed Future Research*

For multi-mode, MD/HD ACI, and MCCI modes:

Develop and improve kinetic models for gasoline-range and diesel-range fuel candidates, BOBs and their blends that can be used to accurately predict combustion behavior at different engine operating modes including the effects of dilution, equivalence ratio, EGR, pressure, and temperature.

Develop/improve/validate PAH/soot models that predict the formation and oxidation of PAH/soot occurring in Multimode and MD/HD ACI engine modes. Determine how PAH and soot formation are affected by fuel composition, yield sooting index (YSI) and particulate matter index (PMI).

Develop kinetic models that accurately predict the NOx promotion/inhibition effect and NOx emissions to ensure accurate simulation of autoignition and NOx emissions occurring in Multimode and Advanced Compression Ignition (MD/HD). Validate the NOx mechanism for NOx production, consumption and emissions.

Identify fuel blend composition fingerprints that indicate the potential for ACI engine performance. Perform automated searches to identify HPF blends in BOBs that provide high phi sensitivity with other fuel properties (e.g. RON & MON) over a pressure/temperature/equivalence ratio/EGR/ range of interest for ACI.

RON: Research Octane Number MON: Motored Octane Number

*Any proposed future work is subject to change based on funding levels.

Summary

F.2.2.2 – Kinetic Mechanism Development

Impact Chemical kinetic models and measurements of highly ranked fuels enable accurate predictions and projections of combustion behavior at MM (SI/ACI), MCCI, and MD/HD ACI operation for a wide range of stoichiometries, pressures, temperatures, and EGR levels

F.2.2.6 – Kinetic modeling of NOx promotion of autoignition

Impact Due to the presence of NO in residual gases and EGR, kinetic models with validated chemistry for NOx promotion will provide more accurate and reliable simulations of engine experiments.

F.2.2.7a – Kinetic models to predict PAH and Soot

Impact Kinetic models with a validated PAH/soot model will provide the AED and TK teams with in-cylinder and engine-out soot predictions needed to evaluate impact of Co-Optima blendstocks on emissions

F.2.2.6a – Identify chemistry controlling synergistic blending and fuel structures that provide these benefits

Impact Allows searches for blendstocks with high performance for RON, OS, phi sensitivity, and other identified autoignition metrics when blended into base fuels (BOBs)

MM: Multi-mode OS: Octane sensitivity (RON-MON)

Technical Back-Up Slides

Mechanism development: main updates to C2-C4 alcohols

- The **initial alcohols chemical kinetic mechanism** is taken from the work of:

S. M. **Sarathy**, P. Oßwald, N. Hansen, K. Kohse-Höinghaus, Alcohol combustion chemistry, Prog. Energy Combust. Sci. 44 (**2014**) 40-102.

- The **thermochemistry of alcohol related species was changed**: alcohol radicals, enols, peroxides, hydroperoxides, ketohydroperoxides, epoxy alcohols.

- The **reaction rate constants need to be updated** mainly for H abstractions by OH• and HO_2 • and low temperature reaction classes, following recent calculations.

  - Isomerization reactions, HO_2 • elimination and enol formation involving β-HOROO• and HOQ•OOH radicals, from **Lizardo-Huerta** et al., Phys. Chem. Chem. Phys. **2016**, 18, 12231-12251.

  - Formation of carbonyl hydroxyalkyl hydroperoxides and OH (i.e. •O2QOOH=KHP+OH) from **Mohamed** et al., J. Phys. Chem. A **2018**, 122, 3626−3639.